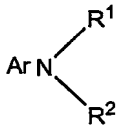
CLAIMS:

1. Use of a combination of diacyl peroxides with an aromatic amine of formula (I):



(I)

where R^1 is an optionally substituted C_1-C_{20} alkyl group, or –(CHR'CHR'-O)$_n$H, where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl;

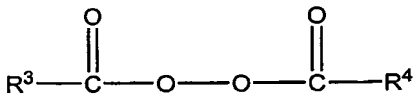
R^2 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H, where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl; and

Ar is an optionally substituted aryl group,

as a redox initiating system in a process for the manufacture of solid polyester granules by suspension polymerisation, wherein the combination of diacyl peroxides comprises diaroyl peroxide and dialkanoyl peroxide having a diaroyl peroxide to dialkanoyl peroxide mole ratio that is equal to or greater than 1:1.

2. The use according to claim 1, wherein one or both of R^1 and R^2 are hydroxyethyl groups.

3. The use according to claim 1 or 2, wherein the diaroyl peroxide is selected from compounds of formula (II):



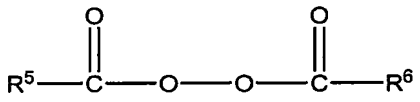
(II)

where R^3 and R^4 are independently selected from optionally substituted aryl.

4. The use according to claim 3, wherein R^3 and R^4 are independently selected from optionally substituted C_6-C_{12} aryl.

5. The use according to any one of claims 1 to 4, wherein the diaroyl peroxide is selected from dibenzoyl peroxide and 2,4-dichlorobenzoyl peroxide.

6. The use according to any one of claims 1 to 5, wherein the dialkanoyl peroxide is selected from compounds of formula (III):



(III)

where R^5 and R^6 are independently selected from optionally substituted alkyl.

7. The use according to claim 6, wherein R^5 and R^6 are independently selected from optionally substituted C_1-C_{20} alkyl.

8. The use according to any one of claims 1 to 7, wherein the dialkanoyl peroxide is selected from dilauroyl peroxide, diacetyl peroxide, disuccinyl peroxide, di(3,5,5-trimethylhexanoyl) peroxide, and didecanoyl peroxide.

9. The use according to any one of claims 1 to 8, wherein the mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 10:1.

10. The use according to claim 9, wherein the mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 5:1.

11. The use according to claim 10, wherein mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 3:1.

12. The use according to any one of claims 1 to 11, wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:8.

13. The use according to claim 12, wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:6.

14. The use according to claim 13, wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:4.

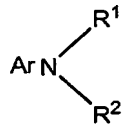
15. The use according to any one of claim 1 to 14, wherein the aromatic amine is selected from N-ethyl-N-hydroxyethyl aniline, N,N-bis hydroxyethyl aniline, N-ethyl-N-hydroxyethyl-p-toluidine and N,N-bis 2-hydroxyethyl)-p-toluidine.

16. A process for the preparation of solid polyester granules comprising:

(i) preparing a solution of unsaturated polyester and a combination of diacyl peroxides in styrene, wherein the combination of diacyl peroxides comprises diaroyl peroxide and dialkanoyl peroxide having a diaroyl peroxide to dialkanoyl peroxide mole ratio that is equal to or greater than 1:1,

(ii) emulsifying said solution in water to provide a stabilised oil-in-water emulsion,

(iii) adding to said emulsion an aromatic amine of formula (I):



(I)

where R^1 is an optionally substituted C_1-C_{20} alkyl group, or –(CHR'CHR'-O)$_n$H, where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl;

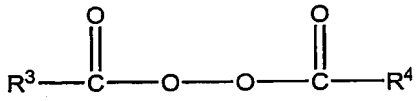
R^2 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H, where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl; and

Ar is an optionally substituted aryl group,

such that reaction of said aromatic amine of formula (I) with each of the diaroyl and dialkanoyl peroxides generates a radical flux capable of initiating polymerisation of the unsaturated polyester and the styrene.

17. The process according to claim 16, wherein one or both of R^1 and R^2 are hydroxy ethyl groups.

18. The process according to claim 16 or 17, wherein the diaroyl peroxide is selected form compounds of formula (II):



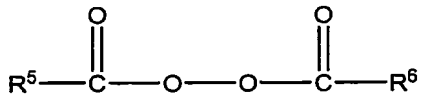
(II)

where R^3 and R^4 are independently selected from optionally substituted aryl.

19. The process according to claim 18, wherein R^3 and R^4 are independently selected from optionally substituted C_6-C_{12} aryl.

20. The process according to any one of claims 16 to 19, wherein the diaroyl peroxide is selected from dibenzoyl peroxide and 2,4-dichlorobenzoyl peroxide.

21. The process according to any one of claims 16 to 20, wherein the dialkanoyl peroxide is selected from compounds of formula (III):



(III)

where R^5 and R^6 are independently selected from optionally substituted alkyl.

22. The process according to claim 21, wherein R^5 and R^6 are independently selected from optionally substituted C_1-C_{20} alkyl.

23. The process according to any one of claims 16 to 22, wherein the dialkanoyl peroxide is selected from dilauroyl peroxide, diacetyl peroxide, disuccinyl peroxide, di(3,5,5-trimethylhexanoyl) peroxide, and didecanoyl peroxide.

24. The process according to any one of claims 16 to 23, wherein the mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 10:1.

25. The process according to claim 24, wherein the mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 5:1.

26. The process according to claim 25, wherein mole ratio of the diaroyl peroxide to the dialkanoyl peroxide ranges from 1:1 to 3:1.

27. The process according to any one of claims 16 to 26 wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:8.

28. The use according to claim 27, wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:6.

29. The use according to claim 28, wherein the mole ratio of the aromatic amine to the total number of moles of the diaroyl and dialkanoyl peroxides ranges from 1:2 to 1:4.

30. The process according to any one of claims 16 to 29 wherein the aromatic amine is selected from N-ethyl-N-hydroxyethyl aniline, N,N-bis hydroxyethyl aniline, N-ethyl-N-hydroxyethyl-p-toluidine and N,N-bis 2-hydroxyethyl)-p-toluidine.

31. The process according to any one of claims 16 to 30, wherein the resultant polyester granule slurry prepared by the process has a residual free styrene level of less than 1000 ppm.

32. The process according to claim 31, wherein the resultant polyester granule slurry prepared by the process has a residual free styrene level of less than 600 ppm.

33. The process according to claim 32, wherein the resultant polyester granule slurry prepared by the process has a residual free styrene level of less than 250 ppm.

34. The process according to any one of claims 16 to 33, wherein the unsaturated polyester is a terpolymer of maleic anhydride, phthalic anhydride and propylene glycol.

35. The process according to any one of claims 16 to 34, wherein the solid polyester granules have an average diameter of up to 500 μm.

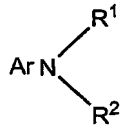
36. The process according to any one of claims 16 to 35, wherein the aromatic amine is added to the emulsion as a spray or as a series of thin streams.

37. A process for the preparation of solid polyester granules comprising:

(i) preparing a solution of unsaturated polyester, and first diacyl and second diacyl peroxide in styrene, wherein the mole ratio of the first peroxide to the second peroxide is equal to or greater than 1:1,

(ii) emulsifying said solution in water to provide a stabilised oil-in-water emulsion,

(iii) adding to said emulsion an aromatic amine of formula (I):



(I)

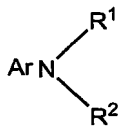
where R^1 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl;

R^2 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H where n is 1 to 10 and each R' is independently selected from H or C_1-C_3 alkyl; and

Ar is an optionally substituted aryl group,

such that reaction of the aromatic amine of formula (I) with each of the first and second diacyl peroxides generates a radical flux capable of initiating polymerisation of the unsaturated polyester and the styrene, and wherein at the commencement of the polymerisation the radical flux generated by the first peroxide is greater than any radical flux generated by the second peroxide.

38. Use of a combination of first diacyl and second diacyl peroxides with an aromatic amine of formula (I):



(I)

where R^1 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H where n is 1 to 10 and each R' is independently selected from H and C_1-C_3 alkyl;

R^2 is an optionally substituted C_1-C_{20} alkyl group, or -(CHR'CHR'-O)$_n$H where n is 1 to 10 and each R' is independently selected from H or C_1-C_3 alkyl; and

Ar is an optionally substituted aryl group,

as a redox initiating system in a process for the manufacture of solid polyester granules by suspension polymerisation, wherein the mole ratio of the first peroxide to the second peroxide is equal to or greater than 1:1, wherein the first and second peroxides are each capable of reacting with the amine to generate a radical flux, and wherein at the commencement of the polymerisation the radical flux generated by the first peroxide is greater than any radical flux generated by the second peroxide.

39. A water-based decorative paint composition comprising binder and polyester granules prepared in accordance with the process of any one of claim 16 to 37, wherein the paint is formulated so that the granules protrude from the surface of an applied paint film.

40. A water-based decorative paint composition comprising binder and pigmented polyester granules, wherein the pigmented polyester granules comprise two or more differently coloured pigmented polyester granules, and wherein the paint is formulated so that the granules protrude from the surface of an applied paint film.

41. The decorative paint according to claim 40, wherein the two or more differently coloured pigmented polyester granules attain their different colours through incorporation of different pigment materials.

42. The decorative paint according to claim 40 or 41, wherein the two or more pigmented polyester granules are prepared in accordance with the process of any one of claim 16 to 37.

43. A water-based decorative paint film comprising pigmented polyester granules, wherein the pigmented polyester granules comprise two or more differently coloured pigmented polyester granules, and wherein the granules protrude from the surface of the paint film.